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Fabrication and Characterization of Nanolayer Capacitors

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Abstract

The miniaturization of high power electronics entails concurrent miniaturization of capacitors since they are typically the largest electronic component. Thin film processing provides a revolutionary approach to make such capacitors smaller. Thin film processing is performed in a vacuum chamber where a reactive sputtering process is integrated with shadow-masking to make nanolayered capacitors. A plasma emission monitor was used to determine the minimum oxygen-to-argon flow ratio for non-absorbing niobium oxides. The electrical characteristics of single-stack capacitors were determined as a function of target voltage and the oxygen-to-argon flow ratio. Deposition rates of the niobium oxides are also presented.

A particular run of single-stack capacitors produced 35 capacitors with an average capacitance of 5.3 ± 0.9 nF and an average dissipation factor of 5.3 ± 1.4 mD. In this run, a capacitor had a maximum breakdown electric field strength of 4.8 MV/cm and an energy density of 31.8 Joules/cc.

Introduction

Over the last decade, Lawrence Livermore National Laboratory has been miniaturizing passive electrical components for high power applications. The picture in Figure 1 exemplifies the footprint reduction of the capacitors over the years from 2.2 cm^2 to 0.48 cm^2. The key factor in component miniaturization is the nano-layered (NL) technology, especially in the fabrication of high-voltage, high-energy density capacitors. The physical vapor deposition process used to apply the various layers of the capacitors in a thin profile will be described; specifically that of the dielectric material niobium oxide. Niobium oxide is a material with a high dielectric constant of 40, and a good candidate for making high-energy density capacitors. The coating process is controlled to minimize particulation and material defect generation in the capacitive device. The NL technology produces rugged capacitors that are all solid-state, compact in volume, monolithic, and with profiles on the order of a micron / nF. Besides military applications, the specific capacitor research may have commercial uses in areas like transportation systems using electric propulsion, utilities, manufacturing controls, consumer appliances and medical equipment.

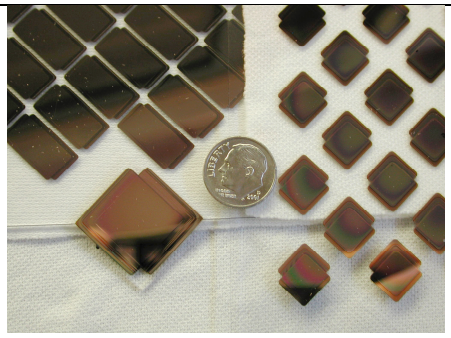

Figure 1. Picture of nanolayer capacitors showing the progression to smaller footprints.

Experimental Set-up

Sputter System

The NL capacitors are made by integrating a reactive sputtering and shadow masking. A layout sketch, looking into the sputter chamber, is shown in Figure 2. Cryo- and turbo-pumps, mounted on the backside of the chamber, were used on the stainless steel chamber to achieve base pressures of 3.3 mPa (4.4E-7 Torr). The sputter pressures are 0.4 (3.0) and 0.93 (7.0) Pa (mTorr) for the metal and oxide depositions, respectively. The substrate and mask assembly was mounted concentrically to the chamber center (annotated as Substrate Table in Fig. 2), and rotated to a specific magnetron gun for the desired material to be sputtered. This method of configuring the substrate conveniently allowed conditioning of the targets on the rear of the substrate fixture.

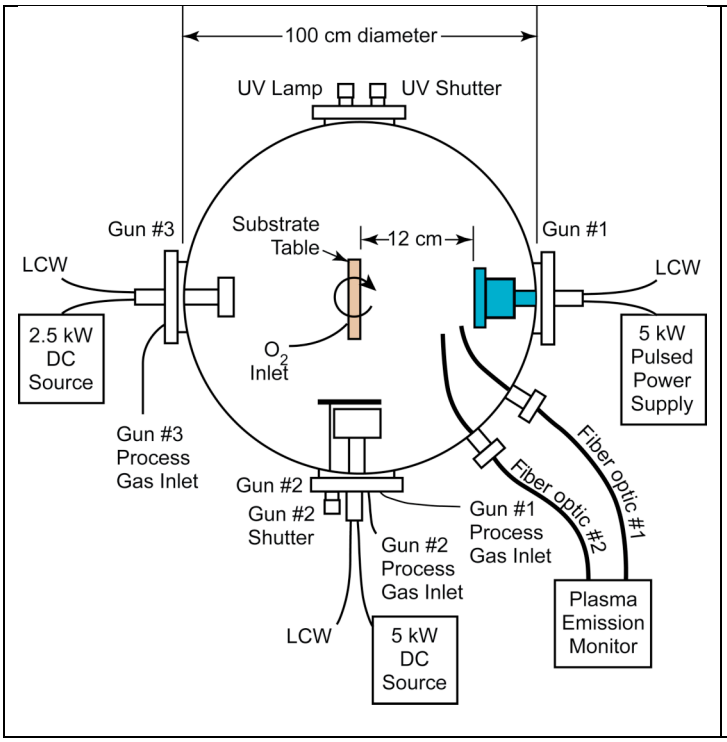

Figure 2. A sketch of the substrate, magnetron, and plasma emission monitoring diagnostic configuration. Gun #1, shaded, is the magnetron containing the Nb target for reactive sputtering of the dielectric oxide. A pulsed DC power supply drives Gun #1. Gun #3 is the magnetron containing the Cu target for deposition of the electrode.

Sputtering is a physical vapor deposition process conducted in a vacuum chamber. A noble gas, typically argon, is used as the plasma carrier medium. A high negative potential is applied across the target material. In magnetron sputtering, this electric field is applied in the presence of a magnetic field to enhance the concentration of and confine the plasma ions near the target surface. Sputtering occurs when the ions accelerate towards and collides with the target, ejecting target material towards the substrate via momentum transfer. For further details of sputtering, the reader is referred to reference [1].

To create an oxide the sputtering is conducted in the presence of an oxygen partial pressure. The primary oxidation reaction of concern occurs on two surfaces, the substrate which is the desirable location and the target which is the undesirable location. Target oxidation decreases the deposition rate which affects throughput and increases the rate of target acing which affects yield. In the LLNL system, the target oxidation is minimized by baffling the oxygen from the target by argon injection inside a can encircling the target (Figure 3). The target arcing is controlled with a commercial pulsed-DC power supply designed to detect and neutralize potential arcs (Figure 2).

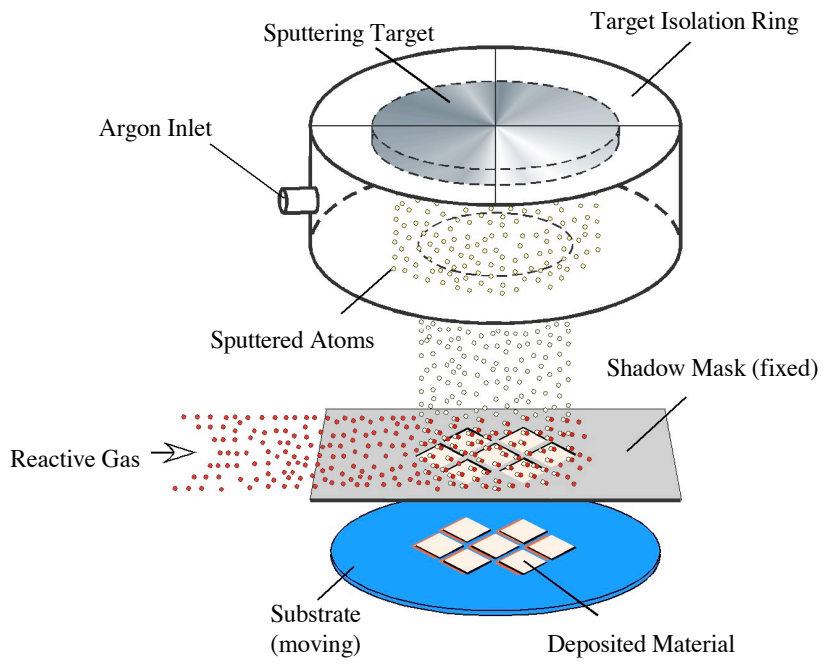

Figure 3. Integrated reactive sputtering process with a shadow mask to make nano-layered capacitors.

Two types of magnetron sputtering sources were used. The electrodes are sputtered with a standard magnetron sputter source. The dielectric oxide is reactively sputtered with a magnetron sputter source built with a rotating magnet array. The rotating magnet array increases the material utilization of the target and the thickness uniformity profile of the coating. The array was rotated at 480 rpm in this study. As a diagnostic of the reactive sputtering process, a plasma emission monitoring (PEM) system was installed. Two fiber optics were used, one to collect the plasma intensity of the Ar ions and the other that of the sputtered metal ions. The two intensities were combined in a ratio to take out the variations of plasma intensity caused by the rotating magnet array. The PEM was used to control the oxygen flow into the chamber, maintaining a constant oxygen-to-metal concentration for the oxidation reaction.

Shadow Mask

A shadow mask is situated between the magnetron source and the substrate. In this case where the mask defines the geometry of the capacitor, it is positioned nearer to the substrate. To separate the electrode and dielectric layers, the substrate is translated linearly with respect to the shadow mask. In three coordinated movements with the magnetrons for coating material, the shadow mask delineates the “minus” electrode, the dielectric, and the “positive” electrode. This sequence cycle can be repeated until the desired number of capacitors have been deposited. The completed device has all the minus electrodes on one side of the capacitor and all the even electrodes at the opposite side, as shown in Figure 4.

Characterization Equipment

The single stack capacitors were tested for capacitance and dissipation factor using a HP-4194A Impedance / Gain-Phase Analyzer. The capacitance values are reported at a 100 KHz test frequency Connections between the capacitor samples and analyzer were made with Inter-Continental Microwave V-Probe manipulators. The high voltage tests were done at a ramp rate of 100 V/sec with a Rod-L M120DC HiPot Tester. Thicknesses were measured on a Veeco DekTak stylus profilometer.

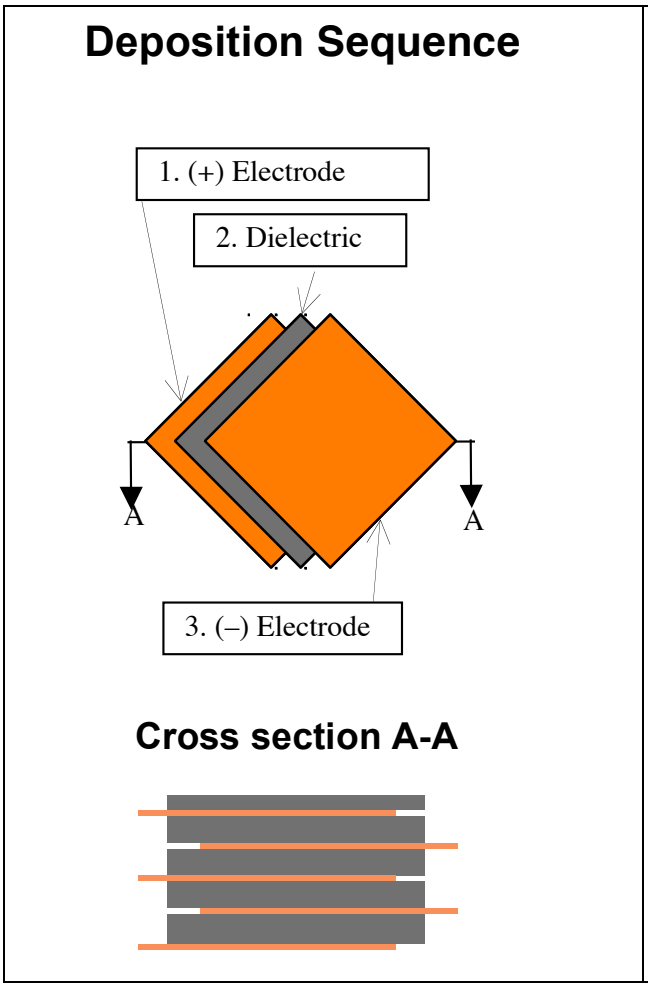

Figure 4 Illustration shows the offsetting of multilayers to generate a nano-layered capacitor. The positive and negative electrodes are connected together on the left and right side of the capacitor, respectively.

Results and Discussion

Fabrication

The electrical performance of a capacitor is linked intrinsically to the quality of the dielectric. For the capacitors here, the dielectric is niobium oxide. In reactive sputtering, an oxygen partial pressure regime can be established with the deposition rate vs reactive gas flow technique. Figure 5 is the reactive sputtering hysteresis curve of plasma emission intensity as a function of oxygen flow during Nb deposition. The plasma emission monitor was tuned to 410 nm wavelength, an intense niobium ion emission line. At zero oxygen flow, the target is in the condition of sputtering with a metallic deposition rate. As the oxygen flow increase from zero to 27 sccm (filled diamonds), the target is slowly oxidized, the oxidized area encroaches into the surface for metallic sputtering, and the ejected niobium metal concentration decreases as indicated by a decrease in the plasma intensity at from 1.0 to 0.7. At an oxygen flow of around 27 sccm, there is a rapid decrease in the normalized plasma intensity from 0.7 to < 0.1. This target condition is called the "fully" oxidized state. The target recovers to the metallic state if one decreases the oxygen flow to zero as indicated in the figure.

The plasma emission monitor was integrated into the control loop of the oxygen mass flow controller in order that oxides could be deposited in the oxygen flow regime of 27 sccm where the target is significantly, but not fully, oxidized. The intent was to find the minimum oxygen flow required to produce the best oxide. Four oxides were reactively sputtered (open diamonds) using feedback control from the plasma emission monitor. The visual quality of the oxides is annotated in the figure, showing that the best oxide, as defined by transparency in the visible regime, is nearly the same as sputtering the niobium target in a fully oxidized state.

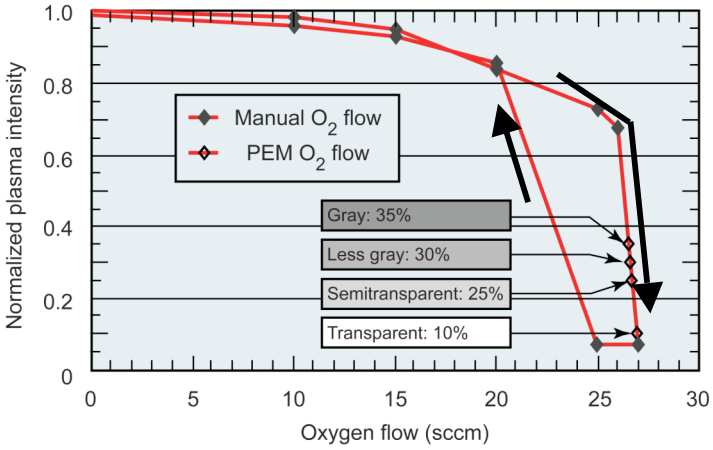

Figure 5. Reactive sputtering hysteresis curve. The plasma intensity at 410 nm, one of the Nb ion emission lines. Arrows indicate direction of oxygen flow change.

Process Variables

Two sputtering process variables were selected to make single layer capacitors for electrical characterization. One variable is the amount of oxygen, represented by the oxygen-to-argon flow ratio. From Figure 5, the minimum ratio is 0.30 and we choose the maximum ratio of 1.0 and a middle ratio of 0.72. The motivation for increasing the oxygen flow (concentration) is to assure as complete an oxidation as possible of the Nb metal species arriving at the substrate. The other variable is the target voltage, which was changed by the power set-point. The motivation here is to increase the average energy of the reaction species, oxygen and Nb, to again assure as complete an oxidation as possible at the surface of the substrate. Figure 5 plots the oxide deposition rate as a function of the target voltage and gas ratios that were used to make the single stack capacitors for electrical characterization.

The oxide deposition rates generally increase with target voltage at fixed gas ratio, and generally increase with lower gas ratios. The former is because the power applied to the target is increasing. The latter is probably because the target is more oxidized at the higher ratios. However, there is an unexplained drop of deposition rate at a target voltage of 660 V and at a 0.72 O_2/Ar flow ratio. The oxide deposition rates are between 0.2 and 0.7 nm/sec in this process space, which means it takes about 4 hrs to make a single stack (nominally 5 nF) capacitor.

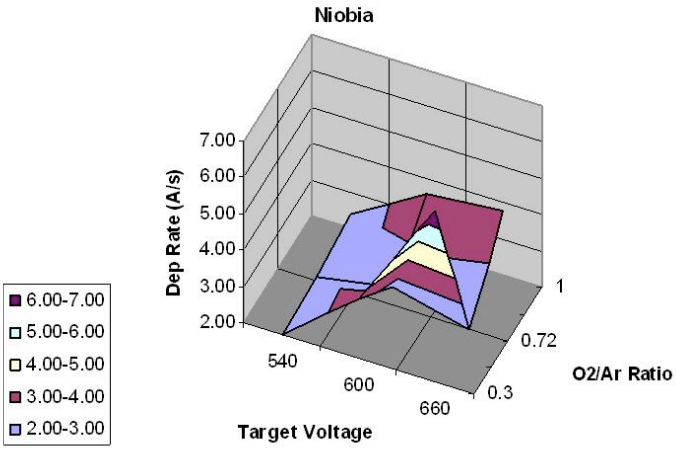

Figure 6 Niobium oxide deposition rates in the target voltage and gas ratio process space.

Electrical properties

Single stack capacitors were made in the process space described above for electrical characterization. The field strength and dissipation factor are given in Figures 7 and 8, respectively. Note that the higher field strengths and lower dissipation factors occur at the lower target voltages and lower gas ratios. The reason for the degraded electrical properties at the high gas ratios were obvious by visual inspection. An excess of gas pressure produced an oxide that scattered light from the roughen the surface of the dielectric. Rough surface contain asperities that lead to low voltage breakdowns. A rough surface is indicative of higher porosities and surface area with the coating. This may contribute to higher DFs because of increased conduction paths along the surface.

At this point there is not a consistent explanation for the capacitors to have a higher field strengths when the target voltage decreases. Other process variables that can affect field strengths is magnetron arcing and cleanliness. Arcing and a heavily coated magnetron tend to spew out debris into the substrate. The debris grows laterally in size with the coating thickness [2] and becomes a likely breakdown path.

A particular run of single-stack capacitors produced 35 capacitors with an average capacitance of 5.3 ± 0.9 nF and an average dissipation factor of 5.3 ± 1.4 mD. In this run, a capacitor had a maximum electric field strength of 4.8 MV/cm and an energy density of 31.8 Joules/cc.

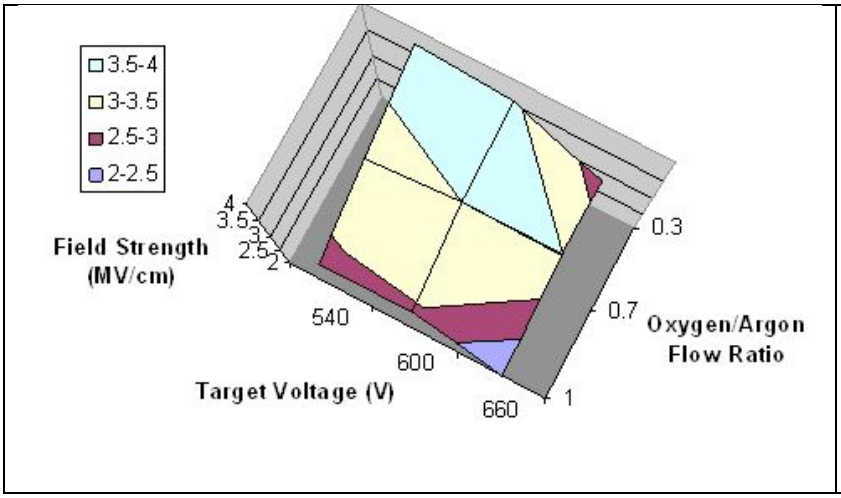

Figure 7 Field strength as a function of target voltages and gas flow ratios.

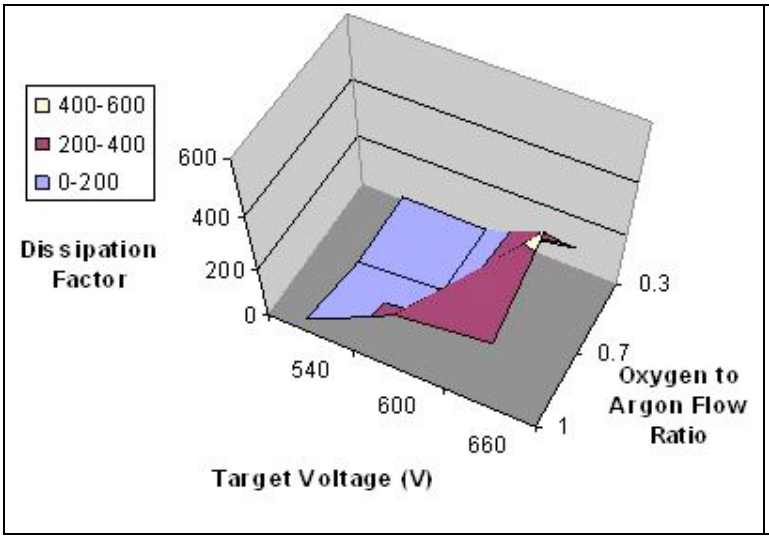

Figure 8 Dissipation Factor as a function of target voltage and gas flow ratio.

Conclusions

A high energy density capacitor was made with a reactive sputter deposition process and shadow masking. The oxygen-to-argon flow ratio appears to be a primary driver of capacitor performance. The best capacitor performance in terms of field strength and dissipation factor was made between these gas ratios of 0.30 and 0.80. At ratios < 0.30, the oxide is absorbing and sub-stoichiometric. At ratios > 0.80, the oxide coating is rough and porous.

Capacitors with high field strengths were produced at target voltages in the 540V regime. This observation is tempered with the fact that other process parameters may affect breakdown voltage. Prepared by LLNL under Contract DE-AC52-07NA27344.

References

1. Milton Ohring, The Materials Science of Thin Films, Academic Press, 1992, chapter 3, sections 6 and 7.

2. Steve Letts, et al, “Ultra-smooth plasma polymerized coatings for laser fusion targets,” J. Vac. Sci. Tech, 19(3), 1981, 739-742.

Biography

Robert Chow has a Ph.D and MS in Materials Science and Engineering from Stanford University, and a BS in Mechanical Engineering from the University of California, Berkeley. His primary experience is in physical vapor deposition of coatings and thin films as applied in semiconductor interconnects, corrosion barriers, laser optics, and, currently in, passive electrical components. Robert has work at Varian Associates and Lawrence Livermore National Laboratory (LLNL). Robert has contributed to national projects such as the Atomic Vapor Laser Isotope Separation, National Ignition Facility, and Weapons programs. He 67 publications and 2 patents.

Alan D. Ellis is a